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TERMINALLY REACTIVE POLYMERS

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This invention relates to improved terminally reactive polymers and to their method of preparation. In another aspect, it relates to a method of curing a polymer which contains terminal aziridinyl groups and to the resulting product.

Uranek, Hsieh and Buck have described in an article in The Journal of Polymer Science, vol. XLVI, 148, 1960, page 535, that polymers having reactive terminal groups can be prepared using an organo alkali metal as a polymerization initiator. The polymer which results from such a polymerization contains alkali metal end groups which can be replaced with more stable reactive end groups by reaction with a suitable reagent. These polymers can then be cured by reaction with polyfunctional organic compounds reactive with the end groups of the polymer. The reactive terminal substituents on the polymer molecules enable a more effective cure since all of the polymer molecule can be tied into the cross-linked structure. The term "telechelic" has been coined to define these terminally reactive polymers and as used in this specification, it refers to a polymer which contains a reactive group upon each end of the molecule. Expressed in another way, telechelic polymers contain at least two terminally reactive groups per molecule. The term "semi-telechelic" is used to refer to a polymer which has a functional group upon only one end of the polymer molecule. This nomenclature can be extended to define the type of telechelic polymer by using the name of the reactive end groups as a prefix, as, for example, carboxy telechelic polymer or carboxy telechelic polybutadiene which is a polybutadiene having a carboxy group upon each end of the polymer molecule.

I have now discovered a new composition which is a polymer of vinylidene-containing compound, said polymer having at least one terminally positioned aziridinyl group per molecule. The preferred compositions of my invention are aziridinyl telechelic polymers such as aziridinyl telechelic polybutadiene. These polymers can be prepared by polymerizing a polymerizable vinylidene-containing monomer in the presence of an organo alkali metal initiator and reacting the resulting polymer containing terminal alkali metal atoms with a polyaziridinyl compound. In another aspect, my invention resides in the cured polymer product which can be made by reacting a polymer of a vinylidene-containing compound having at least one terminally positioned aziridinyl group per molecule with a polyfunctional organic compound having active hydrogen atoms. In a preferred aspect of my invention, an aziridinyl telechelic conjugated diene polymer is cured with a mercapto-substituted carboxy acid. The aziridinyl telechelic polymer can be cured by heat alone or with the above-mentioned polyfunctional organic compounds either with or without auxiliary curatives such as organic peroxides, sulfur or sulfur compounds.

It is an object of my invention to provide a new

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terminally reactive polymer which contains aziridinyl groups. Another object is to provide a method of preparing an aziridinyl telechelic polymer. Still another object is to provide a method of curing a polymer which contains at least one terminally positioned aziridinyl group per molecule. Still another object of my invention is to provide a cured product which is derived by reacting an aziridinyl-telechelic polymer with a polyfunctional organic compound. Other objects, advantages and features of my invention will be apparent to those skilled in the art from the following discussion.

The polymers which contain terminally reactive alkali metal atoms can be prepared from a wide variety of monomers. The preferred monomers are the aliphatic conjugated dienes containing from 4 to 12 carbon atoms per molecule and preferably 4 to 8 carbon atoms per molecule. Examples of these compounds include the following: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 3-methyl-1,3-pentadiene, 1,3-heptadiene, 3-butyl-1,3-octadiene, phenyl-1,3-butadiene and the like. Conjugated dienes containing halogen and alkoxy substituents along the chain can also be employed, such as chloroprene, fluoroprene, 2-methoxy-1,3-butadiene, 2-ethoxy-3-ethyl-1,3-butadiene, and 2-ethoxy-3-methyl-1,3-hexadiene. Conjugated dienes can be polymerized alone or in admixture with each other to form copolymers, or block copolymers. Block copolymers can be prepared from two or more conjugated dienes by charging one compound initially, allowing it to polymerize, and then adding a second conjugated diene and allowing it to polymerize. It is preferred that conjugated diolefins be employed in the practice of my invention and preferred monomers are butadiene, isoprene and piperylene.

In addition to the conjugated dienes I can practice my invention with other monomers containing a $\text{CH}_2=\text{C}<$ group such as the vinyl-substituted aromatic compounds. The vinyl-substituted aromatic compounds include styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, and alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkoxy, aryloxy, and dialkylamino derivatives thereof in which the total number of carbon atoms in the combined substituents is generally not greater than 12. Examples of these aromatic monomers include: 3-methylstyrene (3-vinyltoluene), 4-n-propylstyrene, 4-dodecylstyrene, 4-cyclohexylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 4-(4-phenyl-n-butyl)styrene, 4-methoxystyrene, 3,5-diphenoxystyrene, 4-dimethylaminostyrene, 4-methoxy-6-di-n-propylaminostyrene, 4,5-dimethyl-1-vinylnaphthalene, 8-phenyl-1-vinylnaphthalene, 4-methoxy-1-vinylnaphthalene, 3,6-dimethylamino-1-vinylnaphthalene, and the like. These vinyl-substituted aromatic compounds can be used to form homopolymers or copolymers including block copolymers with each other or with conjugated dienes. The presence of a small amount of polar compound such as the solvent used in preparing the initiator encourages random copolymerization between conjugated dienes and the vinyl-substituted aromatic compounds.

Certain polar monomers can also be polymerized to form homopolymers or copolymers with each other. These polar monomers can be employed to form block copolymers with conjugated dienes and/or vinyl-substituted aromatic compounds. When preparing these block